

# PATENT ABSTRACTS OF JAPAN

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## (54) FIBROUS MAGNETITE AND PRODUCTION THEREOF

### (57)Abstract:

**PURPOSE:** To obtain a fibrous magnetite excellent in carbon dioxide decomposition ability, high in porosity and providing a catalyst free from the degradation of catalytic efficiency due to pressure loss by coating the surface of a fibrous base material with a specific reductive magnetite.

**CONSTITUTION:** The surface of the fibrous base material such as silicon nitride fiber, aluminum nitride fiber or titanium oxide fiber is coated with an oxygen containing iron compound such as magnetite, maghemite by wet process or vapor phase chemical reaction process. Next, by reducing the coated oxygen containing iron compound by hydrogen reduction method or the like, the fibrous magnetite coated with the reductive magnetite expressed by  $\text{Fe}_3\text{O}_4-x$  ( $0 < x \leq 0.5$ ) on the surface of the fibrous base material is obtained. The obtained fibrous magnetite is useful for a catalyst for decomposing carbon dioxide and for a base material for a fuel cell in the case of using a electric conductive one as the fibrous base material.

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CLAIMS

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[Claim(s)]

[Claim 1]Fibrous magnetite which it comes to cover with reduction type magnetite the surface of a fiber base material is indicated to be by  $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ).

[Claim 2]A fiber base material is the whole surface of the surface, or fibrous magnetite of claim 1 which has a carbonaceous layer in part.

[Claim 3]A manufacturing method of fibrous magnetite of claim 1 characterized by returning this oxygenated iron compound after covering the surface of a fiber base material with an oxygenated iron compound.

[Claim 4]A manufacturing method of fibrous magnetite of claim 3 which performs hydrogen reduction.

[Claim 5]Fibrous magnetite which carries out carbon coating of the whole surface or a part of surface fibrous magnetite of claim 1 further.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Industrial Application]**This invention relates to fibrous magnetite. This fibrous magnetite is useful as a catalyst substrate for carbon dioxide decomposition for example. When using for a fiber base material what has conductivity, it is useful also as raw materials, such as a fuel cell, for example.

**[0002]**

**[Description of the Prior Art]**The technical problem in which the recognition over preservation of earth environment increases in recent years that exploitation of clean energy, development, removal of carbon dioxide, reduction, etc. are big, and intermediary \*\*\*\*.

**[0003]**As a method of exploiting clean energy, water is electrolyzed using solar heat and the method of manufacturing hydrogen and oxygen is proposed, for example. However, there are many problems -- installation cost not only becomes immense, but in order to raise the utilization efficiency of solar heat according to this method, need a large-scale plant, therefore a setting position is limited to the ocean, a desert, etc., and international cooperation is required.

**[0004]**The method of collecting carbon dioxide, using amine for example as a method of removing or reducing is proposed. However, by this method, the reuse as resources is impossible and it is deficient in economical added value.

**[0005]**In order to decompose carbon dioxide, using detailed granular material, such as magnetite ( $\text{Fe}_3\text{O}_4$ ) and reduction type magnetite, as a catalyst is studied (the functional material December, 1990 item, JP,3-245845,A, JP,3-285829,A). Although these catalysts have good catalytic activity, the further outstanding thing is demanded. Although there is no method in addition to the solid / gaseous phase system reaction (reaction which specifically lets carbon dioxide pass in this catalyst) for which this \*\*\*\*\* uses a fluid bed under the present circumstances for decomposing carbon dioxide using these catalysts, this method has the fault that pressure loss arises. That is, these catalysts are microscopic particles, and since porosity is low, catalyst efficiency does not fall remarkably or reuse becomes impossible [ cause blinding and solidification with the inflow pressure of carbon dioxide, and ] by solidification. Although the reduction type magnetite which has carbon dioxide resolution superior to magnetite is usually manufactured through hydrogen gas in magnetite, Also in this case, blinding and solidification of magnetite take place with the inflow pressure of hydrogen gas like the above, and there is a problem that reduction of magnetite is not fully performed.

**[0006]**On the other hand, this invention person has proposed the quality of a magnetic matter which covers the surface of a fiber base material with magnetite in JP,62-256800,A and JP,62-260800,A as a raw material for electromagnetic wave shields aiming at the restoration to resin. However, there is no statement about decomposition of carbon dioxide in these gazettes, and there is also no description about reduction type magnetite in them.

**[0007]**

[Problem(s) to be Solved by the Invention]The purpose of this invention has the carbon dioxide decomposition activity which compared with the reduction type magnetite of the above-mentioned conventional particle state, and was remarkably excellent, and since porosity is high, there is in providing the fibrous magnetite which there is no decline in the catalyst efficiency by pressure loss, and can serve as a recyclable catalyst.

[0008]

[Means for Solving the Problem]Namely, fibrous magnetite which comes to cover this invention with reduction type magnetite the surface of (1) fiber base material is indicated to be by  $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ), (2) Provide fibrous magnetite which carries out carbon coating of some or the whole surface of a manufacturing method of fibrous magnetite of the above (1), and the surface of fibrous magnetite of (3) above (1) further.

[0009]Fibrous magnetite of the above (1) is covered with reduction type magnetite the surface of a fiber base material is indicated to be by  $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ).

[0010>About ten to 300 thing of an aspect ratio is [ ten to about 1000 ] usually [ ten or more ] preferably good [ usually / fiber length / 3 micrometers - about 50 mm ] as a fiber base material, although there is no restriction in particular at 10 micrometers - about 30 mm preferably. When fiber length decomposes carbon dioxide in less than 3 micrometers, textiles may break and it may become still shorter, and a fall of catalytic activity by pressure loss may be caused. On the other hand, even if it exceeds 50 mm, there is no problem in particular, but covering of reduction type magnetite may become difficult and improvement in moreover more much more catalytic activity may be unable to be expected. When an aspect ratio becomes remarkably small from ten, there is a possibility that improvement in catalytic activity may become insufficient.

[0011]Although there is no restriction in particular also as construction material which constitutes a fiber base material, if the stability of reduction type magnetite to cover, catalytic activity, etc. are taken into consideration, Alkaline-earth metals, such as alkaline metals, such as Li, Na, and K, Mg, Ca, Sr, and Ba, Group VIA elements, such as IVa group elements, such as Ti and Zr, Mo, W, Fe, Group IIIb elements, such as group Ib elements, such as VII group elements, such as Co, and Cu, B, and aluminum, Halogens, such as group Vb elements, such as IVb group elements, such as C, Si, Sn, and Pb, N, P, and Sb, F, Cl, Br, and I, and these oxides, a hydrogen-containing compound, carbonate, sulfate, etc. can be mentioned, and these at least one sort can be used. Fiber base material of \*\*\*\*\* used by this invention is good at at least one sort of aggregates, such as a mixture of said ingredient, a compound, double salt, a eutectic crystal thing, and micro crystallite, etc., or its \*\*\*\*\* is also good at a single crystal body, for example. As an example of a fiber base material, for example A graphite whisker, carbon fiber, Boron carbide textiles, silicon carbide fiber, titanium carbide textiles, boron nitride textiles, Silicon nitride textiles, aluminum nitride textiles, silicon oxide textiles, titanium oxide textiles, Aluminum oxide textiles, tin oxide textiles, zinc oxide textiles, magnesium oxide textiles, Titanium dioxide fibers, titanitic acid alkali textiles, titanitic acid alkaline earth textiles, Boric acid aluminum textiles, magnesium borate textiles, aluminum silicate textiles, Magnesium silicate textiles, calcium silicate fibers, zinc silicate textiles, calcium phosphate textiles, An alumina fiber, an alumina silica fiber, etc. can be mentioned and silicon nitride textiles, aluminum nitride textiles, silicon oxide textiles, titanium oxide textiles, aluminum oxide textiles, titanitic acid alkali textiles, titanitic acid alkaline earth textiles, boric acid aluminum textiles, etc. are preferred also in it. These textiles may be doped in very small quantities with a different species element, and the surface treatment may be carried out of said ingredient. A substance which has conductivity and catalytic activity of Au, Pt, Ag, nickel, carbon, etc. in these fiber surfaces in accordance with a method of a statement at JP,58-20722,A, for example may be covered.

[0012]In this invention, reduction type magnetite covered on the surface of the above-mentioned fiber base material is shown by empirical formula:  $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ). When x exceeds 0.5, there is a possibility that carbon dioxide decomposition activity may fall. Reduction type magnetite itself is a

compound publicly known as mentioned above, and it is manufactured by returning magnetite ( $\text{Fe}_3\text{O}_4$ ). Although a covering rate in particular to a fiber base material of reduction type magnetite is not restricted but it can choose from a wide range suitably according to specific gravity of a fiber base material to be used, a size of surface area, etc., it is good to usually use about fiber base material / reduction type magnetite = 95 / five to 10/90. When it separates remarkably from the aforementioned range, there is a possibility that the carbon dioxide decomposition activity of a catalyst acquired may fall.

[0013] This \*\*\*\*\* covers an oxygenated iron compound on the surface of a fiber base material first to manufacture this invention fibrous magnetite of the above (1). The aforementioned oxygenated iron compound is publicly known, and usually says magnetite, maghemite, a ferrite, etc.

[0014] Publicly known methods, such as wet process, chemical vapor deposition (CVD), the polyphase depositing method (PVD), and sputtering process, are employable as covering of an oxygenated iron compound, for example.

[0015] For example, what is necessary is just to carry out addition mixing of the equivalent mixed water solution of the 1st iron salt and the 2nd iron salt under existence of urea at a water dispersion of a fiber base material according to wet process. A line intermediary of this reaction is also good under stirring. As iron salt, what the solution may dissolve in a thing which shows neutrality or acidity, and a water-soluble solvent, or can form a stable colloidal dispersion system in this solvent is used. Ferric chloride, ferrous sulfate, iron nitrate, iron hydroxide, iron carbonate, organic iron salt, etc. can be mentioned, and, specifically, these at least one sort can be used, for example. What is necessary is just to usually make it into 0.1 – 70(v/v)% grade with the total quantity of the 1st iron salt and the 2nd iron salt, although iron salt concentration in particular in iron salt solution is not restricted. At less than 0.1%, if there is a possibility that coating volume of iron salt may fall and 70% is exceeded on the other hand, stirring or kneading by a mixer will become difficult, and there is a possibility that workability may fall. What is necessary is just to usually make the amount of the urea used about into 30 to 50 (mole ratio) preferably ten to about 100 to the 2nd iron ion, if the ease of carrying out of generation of an oxygenated iron compound, economical efficiency, etc. are taken into consideration although there is no restriction in particular. Although restriction in particular does not have a reaction condition, either, it is preferred to usually carry out under temperature about 50 \*\* – the boiling point, and it is good 5–12, and to set pH of the system of reaction to 10–12 preferably.

[0016] According to the polyphase depositing method, iron salt solution can be added to a water dispersion of a fiber base material under stirring if needed, and a method of hydrolyzing can be mentioned, for example. Iron salt and its concentration may be the same as that of a case of the above-mentioned wet process. A method of adopting a method publicly known as a hydrolysis method, for example, adding hydrolysis agents, such as alkaline metals, such as Li, K, Na, Ca, Mg, Ba, and Sr, or alkaline-earth metals, etc. can be mentioned. What is necessary is just to usually make it into 0.7 to 6 (mole ratio) grade preferably 0.1 to about eight to iron salt, although what is necessary is just to choose the amount of hydrolysis agent used suitably according to iron salt, a kind of fiber base material, etc. A hydrolysis agent usually remains as it is, or is used with a gestalt of solution. In order to promote hydrolysis, a line intermediary is also good in aeration. Reaction temperature is good to usually consider it as not less than 50 \*\*. An iron system compound may be deposited on the fiber base material surface, and this may be changed to an oxygenated iron compound by heating oxidation.

[0017] Subsequently, by returning an oxygenated iron compound covered by the fiber base material surface, this oxygenated iron compound is changed into reduction type magnetite shown by empirical formula:  $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ), and fibrous magnetite of the above (1) can be obtained.

[0018] As reduction, a hydrogen reduction method, decompression, or a vacuum treating method can be mentioned, for example. Hydrogen reduction is performed by introducing hydrogen gas under

temperature of 100–400 \*\*, after inactive gas, such as gaseous helium, for example, replaces the gaseous phase of the system of reaction containing an oxygenated iron compound covering–fiber base material. What is necessary is just to choose installation time of hydrogen gas suitably according to temperature of the system of reaction, quantity of an oxygenated iron compound covering–fiber base material, etc.

[0019]When changing an oxygenated iron compound into reduction type magnetite, as a fiber base material, If the surface whole surface, a thing which has a carbonaceous layer in part, or the surface uses what was covered with carbon, an oxygenated iron compound will be efficiently changed into reduction type magnetite, and fibrous magnetite outstanding especially from a field of catalytic activity, catalyst efficiency, stability, and reusability moreover will be obtained. Although a reason such an outstanding effect is acquired is not yet clear enough, the surface of a carbonaceous layer is [ very detailed ] uneven, and is considered for specific surface area to increase remarkably. It is good for a fiber base material which has a carbonaceous layer on the surface to have conductivity, to be able to use fibrous magnetite \*(ed) using this fiber base material also as a raw material of a fuel cell, and for thickness of a carbonaceous layer to be 1.0 nm – about 10 micrometers in this case.

[0020]A carbonaceous layer may be formed in fibrous magnetite of this invention all over a part of the surface in order to raise the catalytic activity, reusability, etc. further. A publicly known thing can be used as a carbonaceous material, for example, black lead, graphite, etc. can be mentioned. What is necessary is just to decompose carbon dioxide, for example in accordance with a publicly known method using fibrous magnetite of this invention, in order to form a carbonaceous layer.

[0021]It faces decomposing carbon dioxide using fibrous magnetite of this invention, and a method indicated to a publicly known method, for example, the functional material December, 1990 item, JP,3–245845,A, JP,3–285829,A, etc. can be adopted.

[0022]

[Example]An example, a comparative example, and the example of an experiment are given to below, and let this invention be a still clearer thing.

[0023]5.0 g of ferrous chloride ( $\text{FeCl}_2$ and $6\text{H}_2\text{O}$ , NAKARAI tex company make) was added to the 10–% of the weight solution 136g of manufacture ferric chloride ( $\text{FeCl}_3$ and $6\text{H}_2\text{O}$ , NAKARAI tex company make) of example 1 maghemite covering fibrous material, and it dissolved in it. Titania textiles produced by calcinating 4 potassium–titanate hydrate at 300 \*\* after chloride processing in this solution for 5 hours (18 micrometers of fiber length) After applying the 0.2–micrometer fiber diameter of 5.0 g and making it distribute, the bottom room temperature of stirring took 30 minutes, 200 ml of 1 mol/ml ammonia solutions were added, for 30 minutes, after aging, reduced pressure drying was carried out and filtration, rinsing, ethanol washing, filtration, and the substance 11.04g in which magnetism is shown by dark brown were obtained for the solid. It is a substance which consists of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and a titania when the X diffraction of this is carried out, and is \*\*\*\*\*. It became clear that these substances are 18 micrometers of fiber length and fibrous material with a diameter of 0.3 micrometer, and the mug hematite particle whose path is about 1 nm served as floc which is a diameter of about 10 nm, and formed the homogeneous layer about 0.05 micrometer thick in the surface of titania textiles from SEM observation. Maghemite / titania textiles of this substance (weight ratio) = it is 54.7/45.3 and is \*\*\*\*\*.

[0024]5 g of the above–mentioned maghemite covering titania textiles were lightly filled up with a length of about 10 cm in a quartz tube manufacture 10 mm in inside diameter of fibrous reduction magnetite, and 30 cm in length, and silica wool was filled in both sides and it fixed to them. After filling up a length of 5 mm with linear copper oxide (made by a NAKARAI tex company) and fixing to an outlet side by silica wool furthermore, this was installed in the tubular electric furnace and the helium introducing pipe was connected to the aspirator and the entrance side at the outlet side, respectively. Drawing in with an aspirator, temperature up of the degree of furnace temperature was

carried out for gaseous helium to 700 °C with the sink at 20-ml a rate for /for 2 hours, gaseous helium was passed for 30 more minutes, and helium substitution of the inside of a system was carried out. Removing an aspirator after that and holding the degree of furnace temperature at 300 °C, it replaced with gaseous helium and hydrogen gas was poured at 10-ml a rate for /. At a hydrogen gas introducing initial only by the Japanese smoke by hydrogen gas and the steam which is the resultants of copper oxide being accepted slightly \*\*\*\*\*, Hydrogen gas introduction 30 minutes passed, Japanese smoke became deep, when dew condensation arose near the exit of a quartz tube, hydrogen gas was changed to gaseous helium, heating was stopped, it cooled to the room temperature, and the fibrous material which has a layer of reduction magnetite ( $x=0.2$ ) on the surface was obtained. Reduction magnetite / titania textiles of this fibrous material = it is 53.5/46.5 and is \*\*\*\*\*.

[0025]Except replacing with the check maghemite covering titania textiles of fibrous carbon coating reduction magnetite generation, and not using copper oxide, using the above-mentioned fibrous reduction magnetite, After operated it like the above "manufacture of fibrous reduction magnetite", having performed restoration of this fibrous reduction magnetite, and gaseous helium substitution in a system, having heated at 300 °C, introducing hydrogen gas and passing carbon dioxide for 30 minutes at 10-ml a rate for /100 more%, heating was stopped and it cooled to the room temperature.

[0026]The fibrous reduction magnetite in a quartz tube was changing black, and it was checked that it is the substance in which the detailed carbon particle adhered to the surface from SEM observation and the ultimate analysis by a combustion method. The carbon content of this thing is 0.81 % of the weight, and is \*\*\*\*\*. From carbon adhering by this reaction condition, the generation of reduction magnetite by which carbon coating was carried out is checked.

[0027]800 g of deionized water was made to distribute 5.0 g of example 2 titania textiles (the fiber length of 18 micrometers, fiber diameter of 0.2 micrometer). To these dispersion liquid, the bottom of stirring, 9.9 g of ferrous chloride ( $\text{FeCl}_2$  and  $6\text{H}_2\text{O}$ ), Having raised solution temperature to 80 °C and holding this temperature, after adding 27.0 g of ferric chloride ( $\text{FeCl}_3$  and  $6\text{H}_2\text{O}$ ), and 50 g of urea one by one and making it dissolve, in 5 steps, 30 minutes was required and 150 g of urea was added. Aging was performed under the temperature after the end of addition for 1 hour, it refined like the reference example 1 below, and the substance 16.9g in which magnetism is shown by dark brown was obtained.

[0028]From an X diffraction, this substance is a substance which consists of magnetite ( $\text{Fe}_3\text{O}_4$ ) and a titania, and is \*\*\*\*\*. Magnetite / titania textiles of this substance (weight ratio) = it is 70.4/29.6 and is \*\*\*\*\*.

[0029]Using this substance, it was operated like Example 1 below and the fibrous material which has a layer of reduction magnetite ( $x=0.12$ ) on the surface was obtained. Reduction magnetite / titania textiles of this fibrous material = it is 70.2/29.8 and is \*\*\*\*\*.

[0030]The conductive whisker to which the surface of the potassium titanate whisker was made to carry out chemical vacuum deposition of the carbon 8% as example 3 fiber base material Using [DENTORU BK-300 and the Otsuka Chemical Co., Ltd. make], except adding 20 g of ethanol to the system of reaction further, it was operated like Example 1, and it was black and the substance 10.7g in which magnetism and conductivity are shown was obtained.

[0031]An X diffraction shows that this substance is what consists of maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) and the above-mentioned conductive whisker. According to SEM observation, the surface of this substance is in the state where intermediary \*\*\*\* in which maghemite particles are a little coarser than the thing of Example 1 is almost similar, and it is \*\*\*\*\*. The maghemite / the above-mentioned conductive whisker of this substance (weight ratio) = it is 53.3/46.7 and is \*\*\*\*\*.

[0032]Using this substance, it was operated like Example 1 below and the fibrous material which has a layer of reduction magnetite ( $x=0.15$ ) on the surface was obtained. The reduction magnetite /



conductive whisker of this fibrous material (weight ratio) = it is 51.7/48.3 and is \*\*\*\*\*.

[0033]As example 4 fiber base material, it is carbon fiber. Except using [the Koa Oil Co., Ltd. make, the fiber length of 500 micrometers, and the diameter of 1 micrometer], it was operated like Example 3 and the black substance 10.5g was obtained.

[0034]That it is that to which this substance has an enveloping layer of maghemite on the carbon fiber surface according to an X diffraction, and maghemite/carbon fiber of this substance (weight ratio) = it is 55.4/44.6 and is \*\*\*\*\*. According to SEM observation, in the surface of this substance, the floc of detailed maghemite particles had adhered homogeneously like Example 1.

[0035]Using this substance, it was operated like Example 1 below and the fibrous material which has a layer of reduction magnetite ( $x=0.06$ ) on the surface was obtained. Reduction magnetite / carbon fiber of this fibrous material (weight ratio) = it is 54.4/45.6 and is \*\*\*\*\*.

[0036]It was operated without using titania textiles in the manufacture example 1 of comparative example 1 powdered maghemite, and the maghemite powder 5.9g of 300-mesh passage was obtained.

[0037]14 g was required, in order to become a length of about 3 cm and to be filled up 10 cm, if filled up with the above-mentioned maghemite powder 5g like the manufacture example 1 of reduction magnetite in a quartz tube 10 mm in inside diameter, and 30 cm in length. Silica wool was filled in these both sides, a length of 5 mm was further filled up with line copper oxide at the outlet side, and it fixed by silica wool. Before installing this in a tubular electric furnace, put on a stand, connect a helium introducing pipe to an aspirator and an entrance side at an outlet side, respectively, pass gaseous helium, and a preliminary test \*\*\*\*\* and time, A crack occurs in a maghemite powder packing fraction in some places, it will be in the state where each portion divided by a crack was compressed, introduction of gaseous helium is difficult, and it is \*\*\*\*\*.

[0038]Then, a length of 5 cm was filled up loosely, having reduced the quantity of maghemite powder to 5 g, and unfolding it for a while, and it installed in the tubular electric furnace. Temperature up of the degree of furnace temperature was carried out for gaseous helium to 300 \*\* with the sink at 20-ml a rate for /for 5 hours, gaseous helium was passed for 30 more minutes, and helium substitution of the inside of a system was carried out. Although it was operated like "manufacture of fibrous reduction magnetite" of Example 1 below and hydrogen gas was introduced, it was generated by a lot of steams from the introducing initial, and when generating of a steam stopped in about 10 minutes, copper oxide was returned thoroughly. After introducing hydrogen gas for 30 more minutes, it changed to gaseous helium, heating was stopped, and it cooled to the room temperature.

[0039]When the quartz tube was picked out from the tubular electric furnace and observed, the about 4-5-mm-thick powder layer was made to the pars basilaris ossis occipitalis, and the upper part was emasculated. therefore -- gas contact is insufficient -- \*\*\*\*\* -- things are understood.

[0040]After installed in the electric furnace again, having carried out gaseous helium substitution of the inside of a system like the above, after removing the copper oxide returned from the above-mentioned quartz tube, having heated at 300 \*\*, introducing hydrogen gas and passing carbon dioxide for 30 minutes at 10-ml a rate for /100 more%, heating was stopped and it cooled to the room temperature.

[0041]Although adhesion of the carbonaceous material was observed in the bottom wall side of the quartz tube with which the surface and this layer of a powder layer in a quartz tube touch very slightly, there is no change in the central part of this layer, and it was checked that reduction magnetite is hardly generating.

[0042]It was operated without using titania textiles in the manufacture example 2 in the end of comparative example 2 magnetite powder, and 10.7g was obtained after [ magnetite powder ] 300-mesh passage.

The powder layer had adhered the reduction in the end of magnetite powder to the bottom wall side of the quartz tube with \*\*\*\*\* like the manufacture comparative example 1 of reduction magnetite at the time. Copper oxide was removed from the quartz tube, heating was stopped after order next



line \*\*\*\*, and the helium substitution in a system, introduction (5 hours) of hydrogen gas, and introduction (5 hours) of carbon dioxide were cooled to the room temperature. Although the carbonaceous material had adhered to the surface and the periphery of the powder layer in a quartz tube, a carbon content is 0.3% or less about ultimate analysis about the central part of this layer at \*\*\*\*\* and the time, and it turns out that reduction of magnetite is performed unevenly. When the suction pipe of soda lime was made to pass exhaust gas for 1 minute every 30 minutes and it investigated about the change in the weight of carbon dioxide on the occasion of carbon dioxide introduction, in the whole period of introduction, the increase of weight around 10% was shown. This shows that the reduction magnetite which has sufficient carbon dioxide decomposition activity by reduction becoming uneven is not obtained even if it returns the end of magnetite powder.

[0043]The magnetite covering titania textiles of example 5 Example 1, the magnetite covering carbon fiber of Example 4, and powdered activated carbon are mixed at a rate of 78/20 / 2 (weight ratio), It was made to distribute in ethanol, and filtered through the filter cloth, and the felt-like sheet (40% of porosity) about 1 cm thick was obtained by carrying out suction desiccation. By putting this sheet into a crucible with the product lid made from platinum, heat-treating for 3 hours and subsequently cooling to a room temperature at 350 \*\* in a nitrogen gas atmosphere, within an electric furnace, With the carbon monoxide generated from activated carbon, this magnetite changed into reduction magnetite and the felt-like sheet which mainly consists of fibrous reduction magnetite of this invention was obtained. The porosity of this sheet is 52% and is \*\*\*\*\*.

[0044]The felt-like sheet of about 1 cm in thickness and 45% of porosity was obtained like Example 5 except changing the mixing ratio of the maghemite covering titania textiles of example 6 Example 1, the maghemite covering carbon fiber of Example 4, and powdered activated carbon with 70/25 / 5 (weight ratio). This sheet was operated like Example 5 except making firing time into 5 hours, and the felt-like sheet which consists of fibrous reduction magnetite in which the carbonaceous material adhered to that surface was obtained. The porosity of this sheet is 48% and is \*\*\*\*\*.

[0045]5 g of fibrous reduction magnetite textiles obtained in Example 1 are lightly filled up with a length of about 10 cm in a quartz tube 10 example of experiment 1 mm in inside diameter, and 30 cm in length, After filling silica wool in both sides and fixing to them, this was installed in the tubular electric furnace, the aspirator was connected to the outlet side, and the balloon filled up with the automobile exhaust 1l was connected to the entrance side. When motor exhaust was introduced and the gas of the outlet side was analyzed, drawing in with an aspirator with the degree of furnace temperature of 300 \*\*, it was checked that a constant rate of methane is continuously discharged from an introducing initial.

[0046]Except replacing with automobile exhaust and introducing a steam using the carbon adhesion reduction magnetite textiles obtained in example of experiment 2 Example 2, when it was operated like the example 1 of an experiment, it was checked that a constant rate of hydrogen gas is continuously discharged from an introducing initial. The result also with same thing of Example 4 was obtained.

[0047]

[Effect of the Invention]

(a) According to this invention, the fibrous magnetite which has the carbon dioxide decomposition activity which was efficient and was extremely excellent by the simple method can be provided. If this raw material is used, carbon dioxide can be decomposed and hydrogen and methane of a high grade can be generated.

(b) In textiles shape, since porosity is high, this raw material does not have the fall of catalytic activity, and pressure loss \*\*\*\*\* is excellent also in reusability.

(c) Since the catalytic activity ingredient is thinly covered by the base material surface, this raw material has the high utilization efficiency of this active ingredient.

(d) This raw material which has textiles shape is easy to process it into a textile, a sheet shaped, etc., and abundant in usage patterns.

(e) The use as a raw material of it not only being used as a catalyst for carbon dioxide decomposition but a fuel cell is also possible for this raw material.

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(54) 【発明の名称】 繊維状マグネタイト及びその製造法

(57) 【要約】

【目的】 従来の粒子状の還元型マグネタイトに比し著しく優れた炭酸ガス分解活性を有し、且つ、気孔率が高いので圧力損失による触媒効率の低下がなく再利用可能な触媒となり得る繊維状マグネタイトを提供する。

【構成】 繊維質基材の表面が  $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ) で示される還元型マグネタイトで被覆されてなる繊維状マグネタイト及びその製造法。

## 【特許請求の範囲】

【請求項1】 繊維質基材の表面が $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ) で示される還元型マグネタイトで被覆されてなる繊維状マグネタイト。

【請求項2】 繊維質基材が、その表面の全面又は一部に炭素質層を有する請求項1の繊維状マグネタイト。

【請求項3】 繊維質基材の表面を含酸素鉄化合物で被覆した後、該含酸素鉄化合物を還元することを特徴とする請求項1の繊維状マグネタイトの製造法。

【請求項4】 水素還元を行う請求項3の繊維状マグネタイトの製造法。

【請求項5】 請求項1の繊維状マグネタイトの表面の全面又は一部を、更に炭素被覆してなる繊維状マグネタイト。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、繊維状マグネタイトに関する。該繊維状マグネタイトは、例えば、炭酸ガス分解用の触媒基材として有用である。また繊維質基材に導電性を有するものを用いる場合には、例えば、燃料電池などの素材としても有用である。

## 【0002】

【従来の技術】近年、地球環境の保全に対する認識が高まり、クリーンエネルギーの利用や開発、炭酸ガスの除去や削減などが大きな課題となつてい

【0003】クリーンエネルギーを利用する方法としては、例えば、太陽熱を利用して水を電気分解し、水素及び酸素を製造する方法が提案されている。しかしながら、この方法によれば太陽熱の利用効率を高めるために大規模なプラントを必要とし、従つて設置場所が海洋、砂漠などに限定され、設置コストが莫大になるだけでなく、国際的な協調が要求されるなど問題点が多い。

【0004】炭酸ガスを除去または削減する方法としては、例えば、アミンを用いて回収する方法が提案されている。しかしながら、この方法では資源としての再利用が不可能であり、経済的な付加価値に乏しい。

【0005】更に炭酸ガスを分解するために、マグネタイト ( $\text{Fe}_3\text{O}_4$ )、還元型マグネタイトなどの微細粒状物を触媒として用いることが研究されている(機能材料1990年12月号、特開平3-245845号、特開平3-285829号)。これらの触媒は良好な触媒活性を有しているが、一層優れたものが要望されている。また、これらの触媒を用いて炭酸ガスの分解を行うに当たつては、現状では流動床を用いる固体/気相反応(具体的には該触媒中に炭酸ガスを通す反応)以外に方法がないが、この方法には圧力損失が生ずるという欠点がある。すなわち該触媒が微細粒子で且つ気孔率の低いものであるため、炭酸ガスの流入圧力によつて目詰まりや固化を起し、触媒効率が著しく低下したり或いは固化により再利用ができなくなる。更にマグネタイトよりも優れた

炭酸ガス分解能を有する還元型マグネタイトは、通常マグネタイト中に水素ガスを通して製造されるが、この場合にも前記と同様に水素ガスの流入圧力によつてマグネタイトの目詰まりや固化が起り、マグネタイトの還元が充分に行われないという問題がある。

【0006】一方本発明者は、特開昭62-256800号公報および特開昭62-260800号公報において、樹脂への充填を目的とした電磁波シールド用素材として、繊維質基材の表面をマグネタイトで被覆してなる磁性物質を提案している。しかしながら、これらの公報には、炭酸ガスの分解についての記載はなく、また還元型マグネタイトに関する記述もない。

## 【0007】

【発明が解決しようとする課題】本発明の目的は、上記従来の粒子状の還元型マグネタイトに比し著しく優れた炭酸ガス分解活性を有し、且つ、気孔率が高いので圧力損失による触媒効率の低下がなく再利用可能な触媒となり得る繊維状マグネタイトを提供することにある。

## 【0008】

【課題を解決するための手段】即ち本発明は、(1)繊維質基材の表面が $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ) で示される還元型マグネタイトで被覆されてなる繊維状マグネタイト、(2)前記(1)の繊維状マグネタイトの製造法、及び(3)前記(1)の繊維状マグネタイトの表面の一部又は全面を、更に炭素被覆してなる繊維状マグネタイトを提供するものである。

【0009】上記(1)の繊維状マグネタイトは、繊維質基材の表面が $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ) で示される還元型マグネタイトで被覆されたものである。

【0010】繊維質基材としては、特に制限はないが、通常繊維長が3 $\mu\text{m}$ ~50mm程度、好ましくは10 $\mu\text{m}$ ~30mm程度で、アスペクト比が通常10以上、好ましくは10~1000程度、より好ましくは10~300程度のものがよい。繊維長が3 $\mu\text{m}$ 未満では、炭酸ガスを分解する際などに繊維が折れて更に短くなり、圧力損失による触媒活性の低下を起す可能性がある。一方50mmを超えても特に問題はないが、還元型マグネタイトの被覆が困難になり、しかもより一層の触媒活性の向上が望めない可能性がある。アスペクト比が10より著しく小さくなると、触媒活性の向上が不十分になるおそれがある。

【0011】また繊維質基材を構成する材質としても特に制限はないが、被覆する還元型マグネタイトの安定性、触媒活性などを考慮すると、Li、Na、Kなどのアルカリ金属、Mg、Ca、Sr、Baなどのアルカリ土類金属、Ti、ZrなどのIVa族元素、Mo、WなどのVIa族元素、Fe、CoなどのVII族元素、CuなどのIb族元素、B、AlなどのIIIB族元素、C、Si、Sn、PbなどのIVb族元素、N、P、SbなどのVb族元素、F、Cl、Br、Iなどのハロゲン元素及びこれらの酸化物、含水素化合物、炭酸塩、硫酸塩などを挙げることができ、これらの

少なくとも1種を使用できる。本発明で使用する繊維質基材は、例えば、前記成分の混合物、化合物、複塩、共晶物、微結晶などの少なくとも1種の集合体などであってもよく、或いは単結晶体であってもよい。繊維質基材の具体例としては、例えば、グラファイトウイスキー、炭素繊維、炭化ホウ素繊維、炭化ケイ素繊維、炭化チタン繊維、窒化ホウ素繊維、窒化ケイ素繊維、窒化アルミニウム繊維、酸化ケイ素繊維、酸化チタン繊維、酸化アルミニウム繊維、酸化錫繊維、酸化亜鉛繊維、酸化マグネシウム繊維、二酸化チタン繊維、チタン酸アルカリ繊維、チタン酸アルカリ土類繊維、ホウ酸アルミニウム繊維、ホウ酸マグネシウム繊維、珪酸アルミニウム繊維、珪酸マグネシウム繊維、珪酸カルシウム繊維、珪酸亜鉛繊維、リン酸カルシウム繊維、アルミナ繊維、アルミナ-シリカ繊維などを挙げることができ、その中でも、窒化ケイ素繊維、窒化アルミニウム繊維、酸化ケイ素繊維、酸化チタン繊維、酸化アルミニウム繊維、チタン酸アルカリ繊維、チタン酸アルカリ土類繊維、ホウ酸アルミニウム繊維などが好ましい。これらの繊維は異種元素で微量ドーピングされていてもよく、前記成分で表面処理されていてもよい。また、例えば特開昭58-20722号公報に記載の方法に従い、これらの繊維表面にAu、Pt、Ag、Ni、炭素などの導電性及び触媒活性を有する物質を被覆してもよい。

【0012】本発明において、上記繊維質基材の表面に被覆する還元型マグネタイトは、組成式： $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ) で示されるものである。 $x$ が0.5を越えると、炭酸ガス分解活性が低下するおそれがある。還元型マグネタイト自体は、上述の様に公知の化合物であり、マグネタイト ( $\text{Fe}_3\text{O}_4$ ) を還元することにより製造される。還元型マグネタイトの繊維質基材への被覆割合は特に制限されず、使用する繊維質基材の比重、表面積の大きさなどに応じて広い範囲から適宜選択できるが、通常繊維質基材/還元型マグネタイト=95/5~10/90程度とするのがよい。前記の範囲から著しく外れると、得られる触媒の炭酸ガス分解活性が低下するおそれがある。

【0013】上記(1)の本発明繊維状マグネタイトを製造するに当たっては、まず繊維質基材の表面に含酸素鉄化合物を被覆する。前記の含酸素鉄化合物は公知のものであり、通常マグネタイト、マグヘマイト、フェライトなどを言う。

【0014】含酸素鉄化合物の被覆には、例えば、湿式法、気相化学反応法(CVD)、多相沈積法(PVD)、スパッタリング法などの公知の方法が採用できる。

【0015】例えば湿式法によれば、尿素の存在下、繊維質基材の水分散液に第1鉄塩と第2鉄塩の等量混合水溶液を添加混合すればよい。この反応は攪拌下に行つてもよい。鉄塩としては、その水溶液が中性又は酸性を示

すもの及び水可溶性溶媒に溶解し得るか又は該溶媒中で安定なコロイド分散系を形成し得るものを使用する。具体的には、例えば、塩化鉄、硫酸鉄、硝酸鉄、水酸化鉄、炭酸鉄、有機質鉄塩などを挙げることができ、これらの少なくとも1種を使用できる。鉄塩水溶液中の鉄塩濃度は特に制限されないが、通常第1鉄塩と第2鉄塩の合計量で0.1~70(v/v)%程度とすればよい。0.1%未満では鉄塩の被覆量が低下するおそれがあり、一方70%を越えると混合機による攪拌又は混練が困難になり、作業性が低下するおそれがある。尿素の使用量は特に制限はないが、含酸素鉄化合物の生成のし易さ、経済性などを考慮すると、通常第2鉄イオンに対して10~100程度、好ましくは30~50程度(モル比)とすればよい。反応条件も特に制限はないが、通常50℃~沸点程度の温度下に行うのが好ましく、また反応系のpHを5~12、好ましくは10~12とするのが良い。

【0016】また多相沈積法によれば、例えば、必要に応じ攪拌下にて、繊維質基材の水分散液に鉄塩水溶液を添加し、加水分解を行う方法を挙げることができる。鉄塩及びその濃度は、上記湿式法の場合と同様でよい。また加水分解法としては公知の方法が採用でき、例えば、Li、K、Na、Ca、Mg、Ba、Srなどのアルカリ金属又はアルカリ土類金属などの加水分解剤を添加する方法などを挙げることができる。加水分解剤の使用量は、鉄塩や繊維質基材の種類などに応じて適宜選択すればよいが、鉄塩に対して通常0.1~8程度、好ましくは0.7~6(モル比)程度とすればよい。加水分解剤は通常そのまま又は水溶液の形態で使用される。加水分解を促進するために、エアレーションを行つてもよい。反応温度は、通常50℃以上とするのがよい。さらに、繊維質基材表面に鉄系化合物を沈積させ、これを加熱酸化により含酸素鉄化合物に変化させてもよい。

【0017】次いで、繊維質基材表面に被覆された含酸素鉄化合物を還元することにより、該含酸素鉄化合物が組成式： $\text{Fe}_3\text{O}_{4-x}$  ( $0 < x \leq 0.5$ ) で示される還元型マグネタイトに変換され、上記(1)の繊維状マグネタイトを得ることができる。

【0018】還元法としては、例えば、水素還元法、減圧又は真空処理法などを挙げることができる。水素還元は、例えば、含酸素鉄化合物被覆-繊維質基材を含む反応系の気相をヘリウムガスなどの不活性ガスで置換した後、更に100~400℃の温度下に水素ガスを導入することにより行われる。水素ガスの導入時間は、反応系の温度、含酸素鉄化合物被覆-繊維質基材の量などに応じて適宜選択すればよい。

【0019】含酸素鉄化合物を還元型マグネタイトに変換する時、繊維質基材として、表面の全面又は一部に炭素質層を有するもの又は表面が炭素で被覆されたものを使用すると、含酸素鉄化合物が効率良く還元型マグネタイトに変換され、しかも触媒活性、触媒効率、安定性及

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び再利用性の面から特に優れた繊維状マグネタイトが得られる。この様な優れた効果が得られる理由は、未だ充分明らかではないが、炭素質層の表面は極めて微細な凹凸状態となり、比表面積が著しく増大するためと考えられる。なお表面に炭素質層を有する繊維質基材は導電性を有しており、かかる繊維質基材を用いて製される繊維状マグネタイトは燃料電池の素材としても使用でき、この場合炭素質層の厚みは1.0nm~10μm程度とするのがよい。

【0020】本発明の繊維状マグネタイトには、その触媒活性、再利用性などを一層向上させる目的で、その表面の一部又は全面に炭素質層を形成してもよい。炭素質材料としては公知のものが使用でき、例えば、黒鉛、グラファイトなどを挙げることができる。炭素質層を形成するには、例えば、公知の方法に従い、本発明の繊維状マグネタイトを用いて炭酸ガスを分解すればよい。

【0021】本発明の繊維状マグネタイトを用いて炭酸ガスを分解するに際しては、公知の方法、例えば機能材料1990年12月号、特開平3-245845号、特開平3-285829号等に記載された方法が採用できる。

【0022】

【実施例】以下に実施例、比較例及び実験例を挙げ、本発明を一層明瞭なものとする。

【0023】実施例1

マグヘマイト被覆繊維状物の製造

塩化第2鉄( $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ 、ナカライテクス社製)の10重量%水溶液136gに塩化第1鉄( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 、ナカライテクス社製)5.0gを加えて溶解した。この溶液に、4チタン酸カリウム水和物を塩酸処理後300℃で5時間焼成して得られたチタニア繊維(繊維長18μm、繊維径0.2μm)5.0gを加えて分散させた後、1モル/lのアンモニア水200mlを攪拌下室温で30分を要して添加し、30分間熟成後、固形物を濾別、水洗、エタノール洗浄、濾別、減圧乾燥し、黒褐色で磁性を示す物質11.04gを得た。これをX線回折したところ、マグヘマイト( $\gamma\text{-Fe}_2\text{O}_3$ )とチタニアからなる物質であつた。またSEM観察から、該物質が繊維長18μm、径0.3μmの繊維状物であり、チタニア繊維の表面に、径が約1nmのマグヘマイト粒子が径約10nmの凝集体となり厚さ約0.05μmの均質な層を形成していることが判明した。該物質のマグヘマイト/チタニア繊維(重量比)=54.7/45.3であつた。

【0024】繊維状還元マグネタイトの製造

内径10mm、長さ30cmの石英管内に、上記マグヘマイト被覆チタニア繊維5gを約10cmの長さで軽く充填し、両側に石英綿を詰めて固定した。さらに出口側に線状の酸化銅(ナカライテクス社製)を5mmの長さに充填し、石英綿で固定した後、これを管状電気炉に設置し、出口側にアスピレーター及び入口側にヘリウム導入管をそれぞれ接続した。アスピレーターで吸引しながら、ヘリウムガ

スを20ml/分の割合で2時間流しながら炉内温度を700℃まで昇温し、さらに30分間ヘリウムガスを流して系内をヘリウム置換した。その後アスピレーターを除去し、炉内温度を300℃に保持したまま、ヘリウムガスに代えて水素ガスを10ml/分の割合で流した。水素ガス導入初期には、水素ガスと酸化銅の反応生成物である水蒸気による日煙が僅かに認められるだけであつたが、水素ガス導入30分経過して日煙が濃くなり、石英管の出口付近に結露が生じた時点で水素ガスをヘリウムガスに切替え、加熱をやめ、室温まで冷却し、表面に還元マグネタイト( $x=0.2$ )の層を有する繊維状物を得た。該繊維状物の還元マグネタイト/チタニア繊維=53.5/46.5であつた。

【0025】繊維状炭素被覆還元マグネタイト生成の確認

マグヘマイト被覆チタニア繊維に代えて上記の繊維状還元マグネタイトを用い、且つ酸化銅を用いない以外は、上記「繊維状還元マグネタイトの製造」と同様に操作して、該繊維状還元マグネタイトの充填、系内のヘリウムガス置換を行い、300℃に加熱して水素ガスを導入し、さらに100%炭酸ガスを10ml/分の割合で30分間流した後、加熱を止め、室温まで冷却した。

【0026】石英管内の繊維状還元マグネタイトは黒色に変化しており、SEM観察及び燃焼法による元素分析から、表面に微細な炭素粒子が付着した物質であることが確認された。このものの炭素含量は0.81重量%であつた。この反応条件により炭素が付着することから、炭素被覆された還元マグネタイトの生成が確認される。

【0027】実施例2

チタニア繊維(繊維長18μm、繊維径0.2μm)5.0gを脱イオン水800gに分散させた。この分散液に、攪拌下、塩化第1鉄( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )9.9g、塩化第2鉄( $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ )27.0g、尿素50gを順次加えて溶解させた後、液温を80℃まで上げこの温度を保持しつつ、更に尿素150gを5回に分けて30分を要して添加した。添加終了後同温度下に1時間熟成を行い、以下参考例1と同様に精製し、黒褐色で磁性を示す物質16.9gを得た。

【0028】この物質は、X線回折からマグネタイト( $\text{Fe}_3\text{O}_4$ )とチタニアからなる物質であつた。該物質のマグネタイト/チタニア繊維(重量比)=70.4/29.6であつた。

【0029】この物質を用い、以下実施例1と同様に操作し、表面に還元マグネタイト( $x=0.12$ )の層を有する繊維状物を得た。該繊維状物の還元マグネタイト/チタニア繊維=70.2/29.8であつた。

【0030】実施例3

繊維質基材として、チタン酸カリウムウイスキーの表面に炭素を8%化学蒸着させた導電性ウイスキー〔デントールBK-300、大塚化学(株)製〕を用い、反応系にエタノール20gをさらに加える以外は実施例1と同様

に操作し、黒色で、磁性及び導電性を示す物質10.7gを得た。

【0031】X線回折により、この物質がマグヘマイト( $\gamma\text{-Fe}_2\text{O}_3$ )と上記導電性ウイスキーからなるものであることが判る。またSEM観察によれば、該物質の表面は、マグヘマイト粒子は実施例1のものよりやや粗くなっていたが、ほぼ類似の状態であった。該物質のマグヘマイト/上記導電性ウイスキー(重量比)=53.3/46.7であった。

【0032】この物質を用い、以下実施例1と同様に操作し、表面に還元マグネタイト( $x=0.15$ )の層を有する繊維状物を得た。該繊維状物の還元マグネタイト/導電性ウイスキー(重量比)=51.7/48.3であった。

【0033】実施例4

繊維質基材として、カーボン繊維〔興亜石油(株)製、繊維長500 $\mu\text{m}$ 、径1 $\mu\text{m}$ 〕を用いる以外は実施例3と同様に操作し、黒色物質10.5gを得た。

【0034】X線回折により、この物質がカーボン繊維表面にマグヘマイトの被覆層を有するものであること、及び該物質のマグヘマイト/カーボン繊維(重量比)=55.4/44.6であった。またSEM観察によれば、該物質の表面は実施例1と同様に微細なマグヘマイト粒子の凝集体が均質に付着していた。

【0035】この物質を用い、以下実施例1と同様に操作し、表面に還元マグネタイト( $x=0.06$ )の層を有する繊維状物を得た。該繊維状物の還元マグネタイト/カーボン繊維(重量比)=54.4/45.6であった。

【0036】比較例1

粉末状マグヘマイトの製造

実施例1においてチタニア繊維を用いずに操作を行い、300メツシユ通過のマグヘマイト粉末5.9gを得た。

【0037】還元マグネタイトの製造

実施例1と同様にして、内径10mm、長さ30cmの石英管内に上記マグヘマイト粉末5gを充填すると約3cmの長さになり、10cm充填するためには、14gを要した。この両側に石英綿を詰め、さらに出口側に線状酸化銅を5mmの長さに充填し、石英綿で固定した。これを管状電気炉に設置する前に、架台に乗せ、出口側にアスピレーター及び入口側にヘリウム導入管をそれぞれ接続してヘリウムガスを流して予備試験を行ったところ、マグヘマイト粉末充填部分に所々亀裂が発生し、亀裂によつて分かれた各部分が圧縮された状態となり、ヘリウムガスの導入が困難であった。

【0038】そこで、マグヘマイト粉末の量を5gに減らし、少しはぐしながら5cmの長さにゆるく充填し、管状電気炉に設置した。ヘリウムガスを20ml/分の割合で5時間流しながら炉内温度を300℃まで昇温し、さらに30分間ヘリウムガスを流して系内をヘリウム置換した。以下実施例1の「繊維状還元マグネタイトの製造」と同様に操作して水素ガスを導入したが、導入初期から多量

の水蒸気が発生し、約10分で水蒸気の発生が停止した時点で酸化銅が完全に還元された。さらに30分間水素ガスを導入した後、ヘリウムガスに切替え、加熱をやめ、室温まで冷却した。

【0039】石英管を管状電気炉から取り出して観察したところ、底部に厚さ約4~5mmの粉末層ができ、上部は空洞化していた。よつてガス接触が不十分であったことが判る。

【0040】上記石英管から還元された酸化銅を除いた後、再び電気炉に設置し、上記と同様にして系内をヘリウムガス置換し、300℃に加熱して水素ガスを導入し、さらに100%炭酸ガスを10ml/分の割合で30分間流した後、加熱を止め、室温まで冷却した。

【0041】石英管内の粉末層の表面及び該層が接触している石英管の底部壁面に炭素質物質の付着がごく僅かに認められたが、該層の中心部には変化がなく、還元マグネタイトが殆ど生成していないことが確認された。

【0042】比較例2

マグネタイト粉末の製造

実施例2においてチタニア繊維を用いずに操作を行い、300メツシユ通過のマグネタイト粉末10.7gを得た。

還元マグネタイトの製造

比較例1と同様にしてマグネタイト粉末の還元を行ったところ、粉末層は石英管の底面壁面に付着していた。石英管から酸化銅を取り除き、系内のヘリウム置換、水素ガスの導入(5時間)及び炭酸ガスの導入(5時間)を順次行つた後、加熱を止め、室温まで冷却した。石英管内の粉末層の表面及び周辺部には炭素質物質が付着していたが、該層の中心部について元素分析を行つたところ、炭素含量は0.3%以下であり、マグネタイトの還元が不均一に行われていることが判る。なお、炭酸ガス導入の際に、30分毎に排ガスをソーダ石灰の吸入管に1分間通過させて炭酸ガスの重量の増減について調べたところ、導入の全期間において10%前後の重量増を示した。このことから、マグネタイト粉末を還元しても、還元が不均一になり、充分な炭酸ガス分解活性を有する還元マグネタイトが得られないことが判る。

【0043】実施例5

実施例1のマグネタイト被覆チタニア繊維、実施例4のマグネタイト被覆カーボン繊維及び粉末活性炭を78/20/2(重量比)の割合で混合し、エタノール中に分散させ、濾布により濾別し、吸引乾燥することにより、厚さ約1cmのフェルト状シート(気孔率40%)を得た。このシートを白金製蓋付ルツボに入れ、電気炉内にて窒素ガス雰囲気中で350℃で3時間熱処理し、次いで室温まで冷却することにより、活性炭から発生する一酸化炭素によつて該マグネタイトが還元マグネタイトに変換し、主に本発明の繊維状還元マグネタイトからなるフェルト状シートが得られた。該シートの気孔率は52%であった。

【0044】実施例6



実施例1のマグヘマイト被覆チタニア繊維、実施例4のマグヘマイト被覆カーボン繊維及び粉末活性炭の混合割合を70/25/5（重量比）と変更する以外は、実施例5と同様にして厚さ約1cm、気孔率45%のフェルト状シートを得た。このシートを、焼成時間を5時間とする以外は実施例5と同様に操作し、その表面に炭素質物質が付着した繊維状還元マグネタイトからなるフェルト状シートが得られた。該シートの気孔率は48%であった。

#### 【0045】実験例1

内径10mm、長さ30cmの石英管内に、実施例1で得られた繊維状還元マグネタイト繊維5gを約10cmの長さで軽く充填し、両側に石英綿を詰めて固定した後、これを管状電気炉に設置し、出口側にアスピレーターを接続し、入口側には、自動車排ガス1lを充填した風船を接続した。炉内温度300℃でアスピレーターで吸引しながら自動車排気ガスを導入し、出口側のガスを分析したところ、導入初期から連続的に一定量のメタンガスが排出されていることが確認された。

#### 【0046】実験例2

実施例2で得られた炭素付着還元マグネタイト繊維を用い、自動車排ガスに代えて水蒸気を導入する以外は実験\*

\*例1と同様に操作したところ、導入初期から連続的に一定量の水素ガスが排出されていることが確認された。実施例4のものでも同様の結果が得られた。

#### 【0047】

#### 【発明の効果】

- (a) 本発明によれば、簡易な方法により効率良く、極めて優れた炭酸ガス分解活性を有する繊維状マグネタイトを提供できる。本素材を用いれば、炭酸ガスを分解して高純度の水素やメタンを発生させることができる。
- (b) 本素材は繊維形状で気孔率が高いため、圧力損失ひいては触媒活性の低下がなく、再利用性にも優れている。
- (c) 本素材は、触媒活性成分が基材表面に薄く被覆されているので、該活性成分の利用効率が高い。
- (d) 繊維形状を有する本素材は、布帛、シート状などに加工することが容易であり、利用形態が豊富である。
- (e) 本素材は、炭酸ガス分解用触媒として使用できるだけでなく、燃料電池の素材としての利用も可能である。

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